

Controlling "Injection Barriers" into Prototype Molecular Wires Through Substrate Coupling Chemistry

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The drive to introduce organic molecular materials into electronic device applications (organic or molecular electronics) is motivated by a number of potentially attractive features, such as ease of fabrication, ability to fabricate on flexible substrates, and the wide extent to which organic materials can be functionalized via organic synthetic methods. A range of applications is foreseen for organic field effect transistors and light emitting diodes including, for instance, flexible displays and other low-cost flexible electronics.

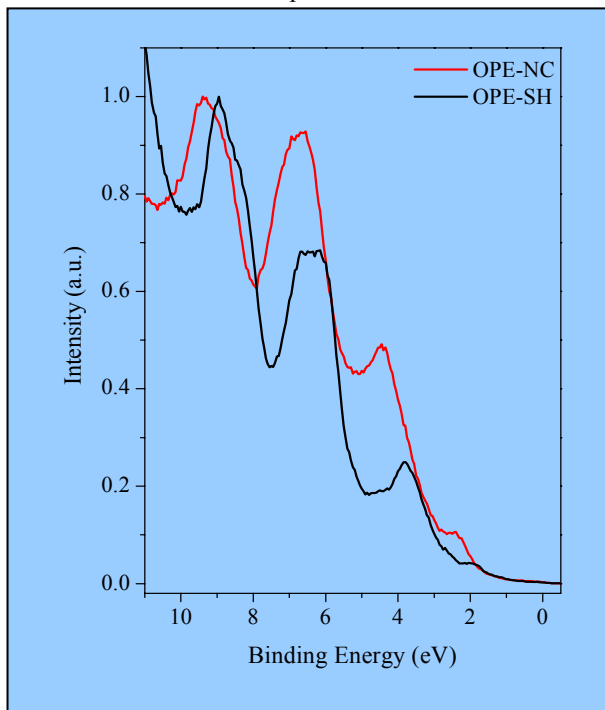
In addition to replacing inorganic semiconductors in more or less conventional device architectures, organic systems are also of interest in the more speculative, and potentially more revolutionary, area of "molecular electronics". Here, it is envisioned that the nonlinear characteristics of individual molecules, or small ensembles, will provide the required device functionality, allowing low-cost chemical synthetic methods to replace, at least partially, multi-billion dollar semiconductor fabrication lines in the production of nanoscale device structures.

In either application format, charge injection at a molecule-contact interface plays a vital role in controlling transport and, thus, potential device performance. Interfacial charge injection is dictated by chemical bonding, and the resulting band line-up between the Fermi level of the contact and transport levels of the molecule. Information relating to band line-up is difficult to obtain using conventional techniques in the case of the single-molecule length-scale systems of interest in molecular electronics. We have employed a combination of one-photon (He I resonance excitation) and two-photon photoelectron spectroscopy, using sub-picosecond Ti:sapphire laser-based excitation, to determine the electronic structure, including injection barriers to both occupied and unoccupied levels, of oligio(p-phenylene-ethynylene)thiol (OPE) self-assembled monolayers, a system that has become a benchmark for theoretical and experimental studies in the area of molecular electronics.

One-photon photoelectron spectra of OPEs adsorbed on Au showing shift in band line-up by varying the linking group from thiol (black line) to isocyanide (red line).

The majority of studies of covalently bound monolayers on metallic surfaces involve thiol-coupling (R-SH) chemistry. Self-assembly of monolayers utilizing thiol chemistry is known to form robust, reproducible monolayers on a variety of metallic surfaces. However, it is important to characterize how the linker group affects the electronic spectra and consequently the band line-up of adsorbed monolayers. Thus, we have undertaken a study of understanding how the band line-up varies as a function of changing the linking chemistry between the molecule and the surface. One-photon photoelectron spectra in the figure shows that the substitution of the thiol-linker for isocyanide (R-NC) in OPEs adsorbed on Au shifts the position of the occupied and unoccupied states relative to the Fermi level by approximately 0.5 eV. Such a large variation will have a major impact on charge injection in molecular systems. Models for important aspects of the bonding in these two systems to Au have been developed that help explain the observed behavior.

This research team will build upon previous studies of understanding the effect molecular structure and linking-group chemistry have on controlling band line-up in covalently bound molecular systems. Our future work will focus on varying the metal onto which the molecule is adsorbed, as well as alkali metal doping of monolayer films.



The results of the CSTL research add important insights to the factors controlling band alignment at metal-organic interfaces, a parameter that plays a critical role in potential applications of organic materials in emerging electronic technologies.